

PATENT SPECIFICATION

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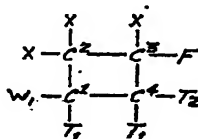
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(54) FIBRE-REACTIVE, WATER-INSOLUBLE DYESTUFFS, PROCESSES FOR THEIR MANUFACTURE AND THEIR USE

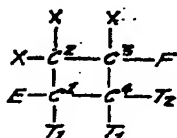
(71) We, FARBWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister, Lucius & Brüning, a Body Corporate recognised under German Law, of 6230 Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, or be particularly described in and by the following statement:—

The present invention provides reactive dyestuffs free from acidic groups conferring solubility in water which contain at least one fibre-reactive acyl residue Z of a halogenated cyclobutane containing a carboxylic acid amide or sulphonic acid amide group bound to the remainder of the dyestuff molecule through the nitrogen atom, especially dyestuffs in which the group Z is a group of the formula



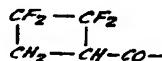
in which T₁ and T₂ each represents a chlorine atom or a cyano or nitro group or a grouping —T', —OT', —COOT'', —SO₂—NT'T'', —SO₂T' or —CO—NT'T'', and the two symbols T₁ can jointly represent a further carbon bond between the carbon atoms C₁ and C₄; T' and T'' each represents a hydrogen atom or an alkyl, aralkyl or aryl group, T''' represents an alkyl or aryl group and X represents a hydrogen or halogen atom, the group Z being bound to the dyestuff molecule through a group —NT'— and through W₁ which represents one of the groupings —CO—, —SO₂—, —SO₂—CH₂—CH₂—, —CO—CH=CH— and —CO—CHT''—CHT', wherein T' and T'' have the meanings given above, and wherein the two T₁ groups and the X atoms may be the same or different. X is preferably a fluorine or chlorine atom.

For introducing the group Z into a dyestuff or a dyestuff component which contains at least one group —NHT', wherein T' has the meaning given above, a compound of general formula

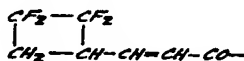


is used wherein T_1 , T_2 and X have the meanings given above and E represents a
 $-\text{CO}-\text{halogen}$, $-\text{SO}_2-\text{halogen}$, $-\text{CH}_2-\text{CH}_2-\text{SO}_2-\text{halogen}$,
 $-\text{CH}=\text{CH}-\text{CO}-\text{halogen}$ or $-\text{CHT}'-\text{CHT}''-\text{CO}-\text{halogen}$ grouping.

The dyestuffs according to the invention contain for example the group Z' of
 formula



or



bound to an amino group.

The invention, for example, provides azo dyestuffs, especially monoazo dyestuffs
 and disazo dyestuffs, anthraquinones, perinones, quinophthalones, styryl dyestuffs and
 nitro dyestuffs.

Azo dyestuffs

The especially interesting dyestuffs include the monoazo dyestuffs of formula
 $\text{D}-\text{N}=\text{N}-\text{A}-\text{NR}_1-\text{R}_2$, wherein D represents the residue of a diazo component, A
 represents an arylene residue, especially an optionally substituted 1,4-phenylene residue,
 R_1 and R_2 each represents an optionally substituted alkyl group, at least one of the
 residues D , A , R_1 and R_2 containing a fibre-reactive residue Z , with Z representing
 the halogenated cycloaliphatic acyl residue defined above.

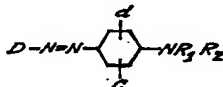
The group A may carry a group $-\text{Z}$ bound *via* an amino group in ortho-position
 to the azo group.

Of particular interest are dyestuffs which correspond to the formula



wherein the alkylene residue contains up to 3 carbons atoms.

Also of interest are monoazo dyestuffs of the formula

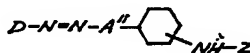


wherein d is a hydrogen atom, a bromine or chlorine atom, a lower alkyl, alkylmercapto
 or alkyloxy residue, a phenoxy, phenylmercapto or phenyl residue which may contain
 as substituents chlorine, bromine, lower alkyl or lower alkoxy residues and c is the
 same or a trifluoromethyl group or a non-fibre reactive acylamino residue wherein the
 acyl residue is derived from a carboxylic acid, an organic monosulphonic acid, a
 carbonic acid mono ester or a carbamic ester, or a fibre-reactive residue $-\text{NH}-\text{Z}$.

Other monoazo dyestuffs to be mentioned are those of the formula

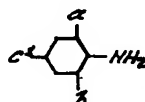


wherein D is a residue of a diazo component and R is a hydroxy-naphthalene residue,
 and those of the formula



wherein D is a residue of a diazo component and A'' is a pyrazolone radical.

The diazo residue D is mainly derived from a monocyclic or bicyclic amine of
 the formula $\text{D}-\text{NH}_2$, for example, from any desired diazotisable heterocyclic amine
 which does not contain any acid substituents which confer solubility in water, but
 especially from an amine which possesses a heterocyclic five-membered ring having
 2 or 3 hetero-atoms, especially a nitrogen atom and one or two sulphur, oxygen or
 nitrogen atoms as hetero-atoms, or from an aminobenzene, especially of formula

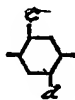


wherein *a* represents a hydrogen or halogen atom or an alkyl or alkoxy, phenoxy, nitro, cyano, carbalkoxy or alkylsulphonyl group, *b* represents a hydrogen or halogen atom or an alkyl, cyano or trifluoromethyl group and *c'* represents a nitro, cyano, carbalkoxy, sulphonic acid amide or alkylsulphonyl group. D may thus represent a heterocyclic diazo component of the thiazole, benzothiazole, imidazole, thiadiazole or isothiazole series or a diazo component of the benzene series.

As examples of such amines there may be mentioned: 2-aminothiazole, 2-amino-5-nitrothiazole, 2-amino-5-methylsulphonyl-thiazole, 2-amino-5-cyanothiazole, 2-amino-4-methyl-5-nitrothiazole, 2-amino-4-methylthiazole, 2-amino-4-phenylthiazole, 2-amino-4-(4'-chlorophenyl)-thiazole, 2-amino-4-(4'-nitrophenyl)-thiazole, 3-aminopyridine, 3-aminoquinoline, 3-aminopyrazole, 3-amino-1-phenylpyrazole, 3-aminoindazole, 3-amino-1,2,4-triazole, 3-amino-5-(methyl-, ethyl-, phenyl- or benzyl-)-1,2,4-triazole, 3-amino-1-(4'-methoxyphenyl)-pyrazole, 2-aminobenzthiazole, 2-amino-6-methylbenzthiazole, 2-amino-6-methoxybenzthiazole, 2-amino-6-chlorobenzthiazole, 2-amino-6-cyanobenzthiazole, 2-amino-6-thiocyanobenzthiazole, 2-amino-6-nitrobenzthiazole, 2-amino-6-carbomethoxybenzthiazole, 2-amino-(4- or 6-methylsulphonyl)-benzthiazole, 2-amino-1,3,4-thiadiazole, 2-amino-1,3,5-thiadiazole, 2-amino-4-phenyl- or -4-methyl-1,3,5-thiadiazole, 2-amino-5-phenyl-1,3,4-thiadiazole, 2-amino-3-nitro-5-methylsulphonylthiophene, 2-amino-3,5-bis-(methylsulphonyl)-thiophene, 5-amino-3-methyl-isothiazole, 2-amino-4-cyano-pyrazole, 2-(4'-nitrophenyl)-3-amino-4-cyanopyrazole, 3- or 4-aminophthalimide, aminobenzene, 1-amino-4-chlorobenzene, 1-amino-4-bromobenzene, 1-amino-4-methylbenzene, 1-amino-4-nitrobenzene, 1-amino-4-cyanobenzene, 1-amino-2,5-dicyanobenzene, 1-amino-4-methylsulphonylbenzene, 1-amino-4-carbalkoxybenzenes, 1-amino-2,4-dichlorobenzene, 1-amino-2,4-dibromobenzene, 1-amino-2-methyl-4-chlorobenzene, 1-amino-2-trifluoromethyl-4-chlorobenzene, 1-amino-2-cyano-4-chlorobenzene, 1-amino-2-carbomethoxy-4-chlorobenzene, 1-amino-2-carbomethoxy-4-nitrobenzene, 1-amino-2-chloro-4-cyanobenzene, 1-amino-2-chloro-4-nitrobenzene, 1-amino-2-bromo-4-nitrobenzene, 1-amino-2-chloro-4-carbomethoxybenzene, 1-amino-2-chloro-4-methylsulphonylbenzene, 1-amino-2-methylsulphonyl-4-chlorobenzene, 1-amino-2-methylsulphonyl-4-nitrobenzene, 1-amino-2,4-dinitrobenzene, 1-amino-2,4-dicyanobenzene, 1-amino-2-cyano-4-methylsulphonylbenzene, 1-amino-2,6-dichloro-4-cyanobenzene, 1-amino-2,6-dichloro-4-nitrobenzene, 1-amino-2,4-dicyano-6-chlorobenzene, 4-aminobenzoic acid cyclohexyl ester, 1-amino-2,4-dinitro-6-chlorobenzene and especially 1-amino-2-cyano-4-nitrobenzene, and also 1-aminobenzene-2-, -3- or -4-sulphonic acid amides such as the N-methylamide or N,N-dimethylamide or N,N-diethylamide.

The diazo components of formula $Z-NR-D'-NH_2$, wherein R represents a hydrogen atom or an alkyl or aralkyl group, for example, a methyl, ethyl or benzyl group, D' represents an optionally substituted phenylene residue and Z has the meaning given above should be especially mentioned.

The group A is preferably the residue of the formula



wherein *c* and *d* each represents a hydrogen atom or a methyl, ethyl, methoxy, ethoxy, phenylthio or phenoxy group.

The group *c* is preferably bound in the ortho-position to the azo group and can in addition to the above-mentioned groups also represent a chlorine or bromine atom, a trifluoromethyl group, an alkylsulphonyl group, preferably a methylsulphonyl group, and an acylamino group which is optionally alkylated, preferably methylated, at the nitrogen atom, in which the acyl residue is the residue of an organic monocarboxylic acid, an organic monosulphonic acid, for example, methanesulphonic, ethanesulphonic or *p*-toluenemonosulphonic acid, or the residue of a carbamic acid or of a carbonic acid monoester or monoamide, for example, phenoxycarbonyl, methoxycarbonyl and aminocarbonyl, or is the residue Z.

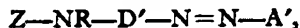
The groups R_1 and R_2 can be hydrogen atoms or lower alkyl groups, that is to say alkyl groups containing 1 to 4, preferably 2 to 4, carbon atoms, for example, methyl, ethyl, *n*-propyl or *n*-butyl groups, which can be substituted in the usual manner, for example, benzyl or β -phenylethyl groups, halogenated alkyl groups, for example, β -chloroethyl, β , β , β -trifluoroethyl or β , γ -dichloropropyl groups, β -cyanethyl groups, alkoxyalkyl groups, for example, β -ethoxyethyl or δ -methoxybutyl groups, hydroxyalkyl groups, for example, β -hydroxyethyl or β , γ -dihydroxypropyl groups, nitroalkyl groups, for example β -nitroethyl groups, carbalkoxy groups, for example, β -carbo(methoxy-, ethoxy- or propoxy)-ethyl groups (in which the terminal alkyl group in the α -position may carry cyano, carbalkoxy, acyloxy and amino groups), or β - or γ -carbo(methoxy- or ethoxy)-propyl groups, acylaminoalkyl groups, for example, β -(acetyl- or formyl)-aminoethyl groups, acyloxyalkyl groups, for example, β -acetoxyethyl, β , γ -diacetoxypropyl, β -propionyloxyethyl or γ -butyryloxypropyl groups, β -(alkyl- or aryl)-sulphonylalkyl groups, for example, β -methanesulphonylethyl, β -ethanesulphonylethyl or β -(*p*-chlorobenzenesulphonyl)-ethyl groups, alkyl- or aryl-carbamoyloxyalkyl groups, for example, β -methylcarbamoyloxyethyl and β -phenylcarbamoyloxyethyl groups, alkyl-oxy-carbonyloxyalkyl groups, for example, β -(methoxy-, ethoxy- or isopropoxy)-carbonyloxyethyl groups, γ -acetamidopropyl, β -(*p*-nitrophenoxy)-ethyl, β -(*p*-hydroxyphenoxy)-ethyl, β -(β' -acetyloxy-carbonyl)-ethyl, β -[(β' -cyano-, hydroxy-, methoxy- or acetoxy-)-ethoxycarbonyl]-ethyl groups, cyanoalkoxyalkyl groups, for example, cyanoethoxy-ethyl, β -carboxyethyl, β -acetylethyl, β -diethylaminoethyl, β -cyanoacetoxyethyl, β -benzoyloxyethyl and β -(*p*-alkoxy- or phenoxy-benzoyloxyethyl groups.

Especially R_1 and/or R_2 may represent a residue of the formula



wherein Z has the meaning given above.

The groups R_1 and R_2 in general contain not more than 18 carbon atoms.
Another preferred type of monoazo dyestuffs has the formula



wherein D' is an optionally substituted phenylene residue and A' the residue of a coupling component, with the exception of phenol or anisole, for example, an enol, an aromatic amine or a pyrazolone. D' is preferably a residue of the formula



wherein *a* and *b* have the meanings given above.

As disazo dyestuffs, there may, for example, be mentioned those disazo dyestuffs in which two identical or mutually different molecules of monoazo dyestuffs of the general type of formula D—N=N—A' , wherein D and A' have the meanings given above and A' can also be a residue of formula $\text{—ANR}_1\text{R}_2$, are bound to one another *via* their coupling components by a divalent bridge Z', either the dyestuff residues or the bridge Z' carrying a residue of formula —NR—Z .

Of particular interest are disazo dyestuffs of the formula



wherein D represents the residue of a diazo component, A is a *p*-phenylene residue that may be substituted and R_1 is an alkyl group that may be substituted.

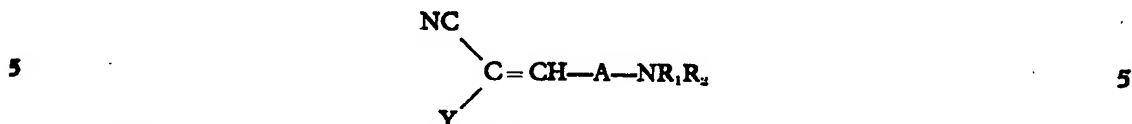
Further, the disazo dyestuffs of the formula



should be mentioned, wherein D', A' and Z have the meanings given above and D'' is an optionally substituted paraphenylene residue.

Styryl dyestuffs

Preferred styryl dyestuffs are those of the formula



wherein A, R₁ and R₂ have the meanings given above and Y is a cyano, carbalkoxy, carboxylic acid amide or arylsulphonyl group, for example, a carbethoxy or phenylsulphonyl group, wherein at least one of the groups A, R₁ and R₂ contains the group —NH—Z. Y may represent the formula

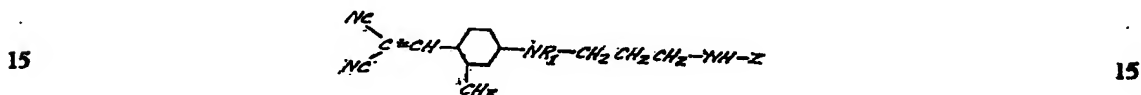


and R₂ has the formula



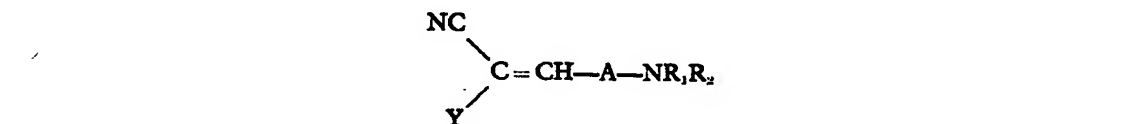
wherein Y represents —O— or —NH—.

The dyestuffs of the formula



wherein the residues R₁ and Z have the meanings given above, are especially preferred.

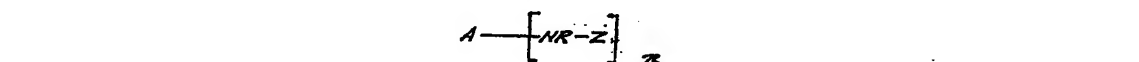
Preferred bis-styryl dyestuffs are those in which two monostyryl dyestuff molecules of the type



which may be identical or different from one another and wherein Y, R₁, R₂ and A have the meanings given above, are bound to one another via the residue A or the group R₁ by a divalent bridge Z', at least one of the residues R₁, R₂, A or Z' carrying a fibre-reactive residue Z.

Anthraquinoid dyestuffs

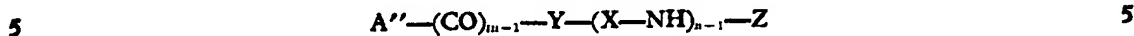
Dyestuffs according to the invention of the anthraquinone series are, for example, anthraquinone derivatives of the formula



wherein n represents 2 or preferably 1, R and Z have the meanings given above and A represents an anthraquinone residue having 3 or 4 condensed rings which contain one or more other substituents, for example, halogen atoms, for example, fluorine, chlorine or bromine, hydroxyl groups, alkoxy groups, amino groups, acylamino groups, alkylamino groups containing 1 to 3 carbon atoms, acyloxy groups, optionally substituted aryl residues, optionally substituted heterocyclic residues, arylamino groups wherein the aryl residue is preferably a phenyl group which can be substituted by one or more halogen atoms, alkyl or alkoxy groups, alkylsulphonyl or optionally substituted phenylsulphonyl groups, alkylthioether or optionally substituted phenylthioether residues as well as nitro, cyano, carboxylic acid ester and acetyl groups. Examples of tetracyclic anthraquinone residues are 1,9-isothiazolanthrone, 1,9-anthrapyrimidine or 1,9-pyrazolanthrone. Alkyl residues are preferably lower alkyl residues which can contain up to 6 carbon atoms. Of particular interest are those dyestuffs which correspond to the formula



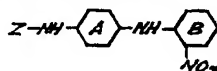
wherein n is 1 or 2, Z has the meaning given above and A' represents a residue of the anthraquinone series having 3 to 5 condensed rings, which contain one or more other substituents, and R is a hydrogen atom or an alkyl group and those which correspond to the formula



wherein n is 1 or 2, m is 1 or 2, A'' is an anthraquinone, thiazoleanthrone, pyrazoleanthrone or phthaloylacridone, X is alkylene or arylene, and Y is $-O-$ or $-NH-$; with the proviso that the $-CO-$ can be attached only in a β -position of the anthraquinone nucleus.

Nitro dyestuffs

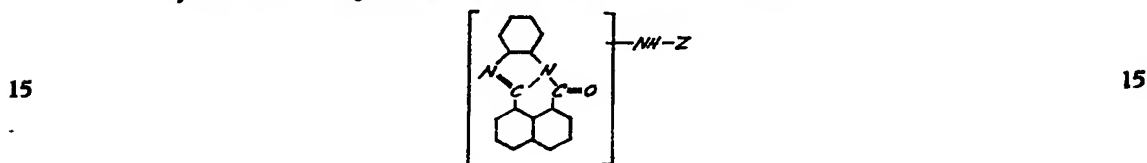
Dyestuffs according to the invention are those of the formula 10



wherein the nucleus B may be substituted.

Perinone dyestuffs

Dyestuffs according to the invention are those of the formula



which may be substituted.

The new dyestuffs may be manufactured for example a) by reacting a dyestuff which contains at least one group of the formula $-NHR$, wherein R has the meaning given above, with at least one acid halide of a halogenated cyclobutane derivative of the formula $Z-Hal$, wherein Hal is a halogen atom, or b) by linking 2 components of which at least one component contains at least one group Z bound to an amino group, by condensation or coupling, to give a dyestuff which contains at least one group Z which has the meaning given above in each case. 20

The invention therefore provides a process for the manufacture of reactive dyestuffs wherein either a diazotised amine is coupled with a coupling component and one of the two components contains at least one of the fibre-reactive groups indicated in Claim 1, or a dyestuff containing an acylatable amino group is acylated with an anhydride or halide of a carboxylic or sulphonic acid containing a halogenated cyclobutane ring. 25

I) Process Variant a) 30

A. Fibre-reactive acylating agents

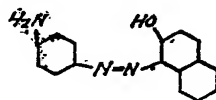
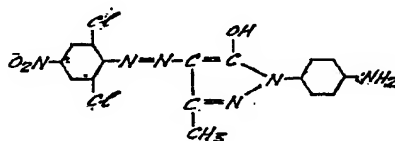
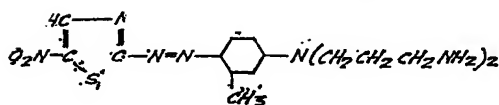
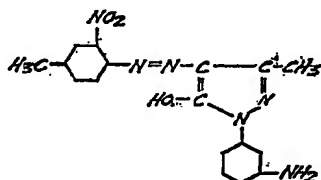
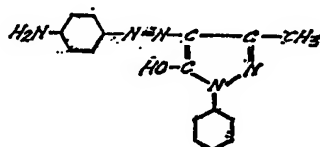
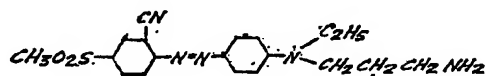
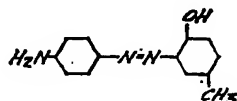
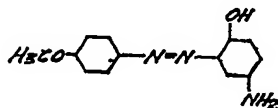
As fibre-reactive acylating agents which introduce the residue Z , the acid halides or anhydrides may be used, for example: 2,2,3,3-tetrafluorocyclobutanecarboxylic acid chloride-1, 2-chloro-2,3,3-trifluorocyclobutanecarboxylic acid chloride-1, 2,2-dichloro-3,3-difluorocyclobutanecarboxylic acid chloride-1, 1-chloro-2,2,3,3-tetrafluorocyclobutanecarboxylic acid chloride-1, 1,2-dichloro-2,3,3-trifluorocyclobutanecarboxylic acid chloride-1, 1,2,2-trichloro-3,3-difluorocyclobutanecarboxylic acid chloride-1, 2,2,3,3-tetrafluorocyclobutanecarboxylic acid chloride-1, 2,2,3,3-tetrafluorocyclobutanecarboxylic acid chloride-1, 1-methyl-2,2-dichloro-3,3-difluorocyclobutanecarboxylic acid chloride-1, 2,2,3,3-tetrafluoro-4,4-dimethylcyclobutanecarboxylic acid chloride-1, 2-chloro-2,3,3-trifluoro-4-phenylcyclobutanecarboxylic acid chloride-1 and 3-(2',2',3',3'-tetrafluorocyclobutyl)-acrylic acid chloride. 35

B. Dyestuff components

The following dyestuffs are for example suitable as reactive components:

1) Azo dyestuffs 45





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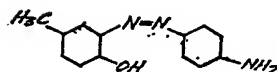
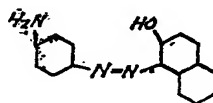
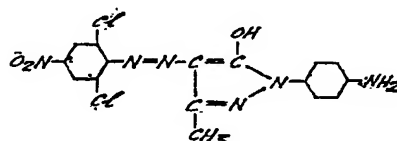
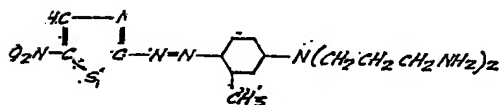
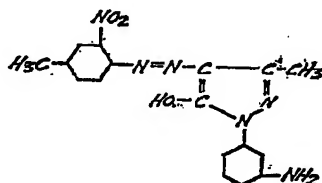
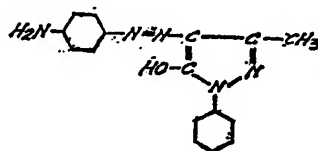
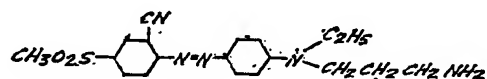
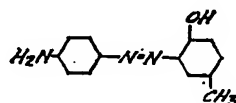
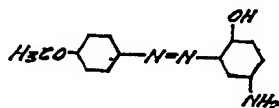
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2) Anthraquinone dyestuffs

1,4-Diaminoanthraquinone, 1-amino-4-hydroxyanthraquinone, 1,4-bis-(p-amino-anilino)-5-hydroxyanthraquinone, 1,4-bis-(p-amino-anilino)-5,8-dihydroxyanthraquinone, 1,4-bis-(p-amino-anilino)-2-methylanthraquinone, 1,5-bis-(p-amino-anilino)-4,8-dihydroxyanthraquinone, 1-hydroxy-4-(p-amino-anilino)-anthraquinone, 5-amino-

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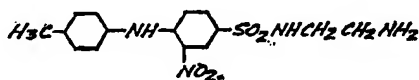
2) Anthraquinone dyestuffs

1,4-Diaminoanthraquinone, 1-amino-4-hydroxyanthraquinone, 1,4-bis-(p-amino-anilino)-5-hydroxyanthraquinone, 1,4-bis-(p-amino-anilino)-5,8-dihydroxyanthraquinone, 1,4-bis-(p-amino-anilino)-2-methylantraquinone, 1,5-bis-(p-amino-anilino)-4,8-dihydroxyanthraquinone, 1-hydroxy-4-(p-amino-anilino)-anthraquinone, 5-amino-

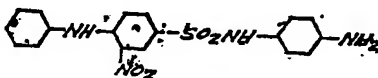
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1,9-isothiazolanthrone, 4-amino-1,9-anthrapyrimidine, 5-amino-1,9-anthrapyrimidine, 2- or 3-aminobenzanthrone and 5- or 8-amino-1,9-pyrazolanthrone.

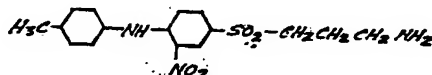
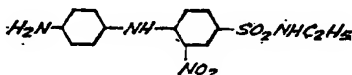
3) Nitro dyestuffs



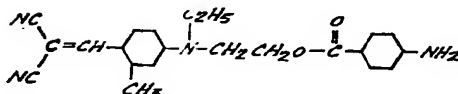
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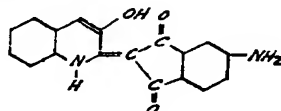
4) Styryl dyestuffs



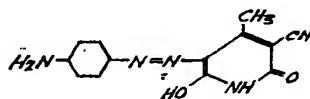
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5) Quinophthalone dyestuffs

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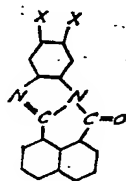


6) Pyridone dyestuffs



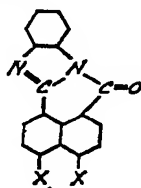
7) Perinone dyestuffs

15



15

or the mixtures of the dyestuffs of formula



wherein one X represents a group of formula —NH_2 and one X represents a hydrogen atom.

C) Reaction conditions

The reaction with the acylating agent generally takes place by adding the acid halide to the amine to be acylated, the process in most cases being carried out in an organic solvent, for example, methylene chloride, chloroform, carbon tetrachloride, benzene, a chlorinated benzene, a chlorinated higher aromatic hydrocarbon, diisopropyl ether, dioxane, acetonitrile, glacial acetic acid and 80% acetic acid, or in an acid aqueous solution or with a suspension of the dyestuff to be acylated.

II) Process variant b)

A. Azo dyestuffs (coupling)

The azo dyestuffs according to the invention can, for example, be obtained by coupling a diazonium compound of an amine with a coupling component, at least one of the components having a fibre-reactive group Z.

1) Diazo components

Suitable diazo components which contain the fibre-reactive group Z are obtained by acylation of an aromatic or heterocyclic nitro compound which possesses at least one group of formula —NHR , for example, 2-amino-4-methylsulphonylnitrobenzene, 4-amino-2-methylsulphonylnitrobenzene or 2,6-dichloro-4-aminonitrobenzene with a fibre-reactive acid chloride of formula Z—Hal , wherein Hal is a halogen atom, and subsequent reduction of the nitro group.

Suitable aromatic diamines may also be acylated, for example, para-phenylenediamine, with one equivalent of the fibre-reactive acid chloride of the formula Z—Hal .

As diazo components *without* a fibre-reactive group Z the above-mentioned diazo components of formula D—NH_2 may also be used.

2) Coupling components

Suitable coupling components which contain a fibre-reactive group Z may be obtained as described in our co-pending Application No. 34046/70 (Serial No. 1,293,558) for example by reaction of one of the following components with an acid halide of formula Z—Hal : 3-amino-N,N-bis- β -acetoxyethyl-aniline, 3-amino-N,N-bis- β -cyanoethyl-aniline and N-(γ -aminopropyl)-N-ethyl-aniline.

As coupling components *without* a fibre-reactive group Z there may, for example, be mentioned: N-(β -cyanoethyl)-N-methylaminobenzene, N,N-di- β -hydroxyethylaminobenzene, 1-(N- β -cyanoethyl-N-ethylamino)-3-methylbenzene, 2-hydroxy-3-carboxynaphthalene-o-aniside, 1-(N- β -cyanoethylamino)-3-methylbenzene, 1-(N,N-di- β -hydroxyethyl-amino)-3-thiocyanatobenzene, N- β -cyanoethyl-naphthasultam-(1,8), 1-N,N-di- β -cyanoethylamino)-3-methylbenzene, N-(β -cyanoethyl)-N-(β -hydroxyethyl)-aminobenzene, N-(β -cyanoethyl)-2-methyl-indole, N-(β -cyanoethyl)-tetrahydroquinoline, N-phenyl-aminobenzene, 4-hydroxy-1-methylisoquinoline, 1-hydroxy-3-methylbenzene, 8-hydroxyquinoline, 3-cyano-2,6-dihydroxy-4-methylpyridine, 1,3-dihydroxybenzene, 2-naphthylamine-5-sulphomethylamide, 1-hydroxy-3-cyanomethylbenzene, 1-phenyl-3-methyl-5-pyrazolone and acetoacetic acid ethyl ester.

3) Diazotisation and coupling

The diazotisation of the diazo components mentioned can take place according to methods which are in themselves known, for example, with the aid of mineral acid and sodium nitrite or for example by means of a solution of nitrosylsulphuric acid in concentrated sulphuric acid.

The coupling can also be carried out in a manner which is in itself known, for example, in a neutral to acid medium, optionally in the presence of sodium acetate or a similar buffer substance or catalyst which influences the coupling speed, for example, dimethylformamide, pyridine or one of its salts.

The coupling also takes place advantageously with the components being combined in a mixing nozzle. By this there is to be understood a device in which the liquids to be mixed are combined with one another in a relatively small space, with at least one of the liquids, preferably under elevated pressure, being passed through a nozzle. The mixing nozzle can, for example, be constructed, and operate, according to the principle of the water jet pump, with the supply of one of the liquids into the mixing nozzle corresponding to the supply of water in the water jet pump and the supply of the other liquid into the mixing nozzle corresponding to the connection of the water jet

pump to the vessel which is to be evacuated, it being possible for this latter liquid also to be supplied under elevated pressure.

However, other suitable devices can also serve for the rapid, optionally continuous, thorough mixing.

III) Use

The new water-insoluble dyestuffs, mixtures thereof and their mixtures with other azo dyestuffs are excellently suited to dyeing and printing leather, wool, silk and especially synthetic fibres, for example, acrylic or acrylonitrile fibres, polyacrylonitrile fibres and fibres of copolymers of acrylonitrile and other vinyl compounds, for example, acrylic esters, acrylamides, vinyl-pyridine, vinyl chloride or vinylidene chloride, copolymers of dicyanethylene and vinyl acetate, and of acrylonitrile block copolymers, fibres of polyurethanes, basically modified polyolefines, for example, polypropylene, cellulose triacetate and 2½-acetate and especially fibres of polyamides, for example, nylon-6, nylon-6,6 or nylon-12 and of aromatic polyesters, for example those of terephthalic acid and ethylene glycol or 1,4-dimethylcyclohexane, and copolymers of terephthalic acid and isophthalic acid and ethylene glycol.

The present invention, thus, also provides a process for dyeing or printing cellulose-containing fibres, especially cotton, wool and synthetic fibres, especially fibres containing amine and/or amide groups, wherein there are used reactive dyestuffs free from acidic groups conferring solubility in water which contain at least one fibre-reactive acyl residue Z of a halogenated cyclobutane containing a carboxylic acid amide or sulphonic acid amide group bound to the remainder of the dyestuff molecule through the nitrogen atom.

For dyeing in aqueous liquors, the water-insoluble dyestuffs are advantageously used in a finely divided form and dyeing carried out with the addition of a dispersing agent, for example, sulphite cellulose waste lye or of synthetic detergents or a combination of various wetting agents and dispersing agents. As a rule, it is advantageous to convert the dyestuff to be used, before dyeing, into a dyeing preparation which contains a dispersing agent and finely divided dyestuff in such a form that on dilution of the dyestuff preparation with water a fine dispersion is produced. Such dyestuff preparations can be obtained by a method known *per se*, for example, by grinding the dyestuff in a dry or wet form with or without the addition of dispersing agents during the grinding process.

The new dyestuffs dye fibres containing amino groups and/or amide groups, especially wool, from a weakly alkaline, neutral or especially weakly acid bath, for example from a bath containing acetic acid. In certain cases it is advisable, in order to obtain even dyeings on wool, to add polyglycol ether derivatives to the liquor which on average contain at least ten $-\text{CH}_2-\text{CH}_2-\text{O}-$ groups and are derived from monoamines which contain an aliphatic hydrocarbon residue with at least 20 carbon atoms. As a special advantage of the new dyestuffs it should be mentioned that they dye nylon fibres satisfactorily in a very wide pH-range, from acid to alkaline pH-values.

The dyeings and prints obtained with these dyestuffs on polyamide fibres and wool show excellent wet fastness properties, especially good fastness to light, washing, perspiration, fulling and water.

The new compounds are also especially suitable for dyeing fully synthetic fibres for example polyester or nylon fibres from organic solvents, for example from perchlorethylene with or without the addition of 10% of dimethylformamide.

In order to achieve intense dyeings from an aqueous medium on polyethylene terephthalate fibres, it is advantageous to add a swelling agent to the dyebath or to carry out the dyeing process under pressure at temperatures above 100°C, for example at 120°C. Suitable swelling agents are aromatic carboxylic acids, for example, salicylic acid, phenols, for example, *o*- or *p*-hydroxydiphenyl, aromatic halogen compounds for example *o*-dichlorobenzene, or diphenyl.

For heat-fixing the dyestuff, the padded polyester fabric is heated, advantageously after prior drying, for example in a warm stream of air, to a temperature of above 100°C, for example within the range of from 180 to 210°C.

The dyeings obtained according to the present process can be subjected to an after-treatment, for example by heating with an aqueous solution of a non-ionic detergent.

Instead of being applied by impregnation, the indicated dyestuffs can, according to the present process, also be applied by printing. For this purpose a printing ink is for example used which in addition to the auxiliary agents usual in printing, for example, wetting agents and thickeners, contains the finely dispersed dyestuff.

Strong dyeings and prints of good fastness properties are obtained according to the present process.

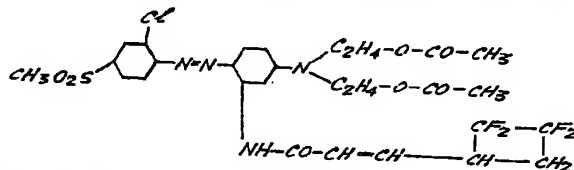
The new water-insoluble dyestuffs can also be used for the spin-dyeing of polyamides, polyesters and polyolefines. The polymer to be dyed is appropriately mixed in the form of powders, granules or chips, as a finished spinning solution or in the fused state, with the dyestuff which is introduced in the dry state or in the form of a dispersion or solution in an optionally volatile solvent. After homogeneous distribution of the dyestuff in the solution or melt of the polymer, the mixture is converted, for example, into fibres, yarns, monofilaments or films by a method known *per se*, by casting, pressing or extruding.

The following Examples illustrate the invention. The parts denote parts by weight and the percentages, percentages by weight unless otherwise stated. The relationship of the parts by weight to parts by volume is the same as that of the gram to the millilitre.

Example 1

1.4 Parts of sodium nitrite are introduced into 30 parts by volume of sulphuric acid and the mixture stirred for 30 minutes. 4.11 Parts of 4-amino-3-chlorophenyl-methylsulphone are introduced at a temperature of 20 to 25°C and the mixture stirred for some time. Thereafter the excess of nitrite is destroyed with urea.

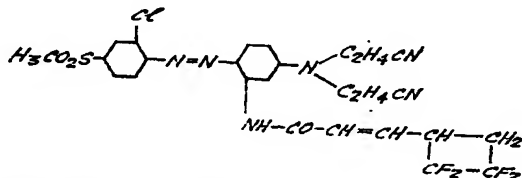
This solution is added dropwise at a temperature of at most 10°C to a solution of 9.2 parts of N-bis-β-acetoxyethyl-3-[β-(2',2',3',3'-tetrafluorocyclobutyl-acryl)-amido]-aniline in 125 parts of 80% acetic acid, the mixture is stirred overnight at 0 to 10°C and the dyestuff is precipitated by adding ice water. After filtering, the dyestuff is washed until neutral and dried *in vacuo*. A dyestuff of the formula



is obtained which dyes nylon fibres orange shades of excellent fastness to washing.

Example 2

When instead of the above-mentioned N-bis-β-acetoxy-ethyl-3-[β-(2',2',3',3'-tetrafluorocyclobutyl-acryl)-amido]-aniline, 7.9 parts of N-bis-β-cyanethyl-3-[β-(2',2',3',3'-tetrafluorocyclobutyl-acryl)-amido]-aniline are used, a dyestuff of the formula

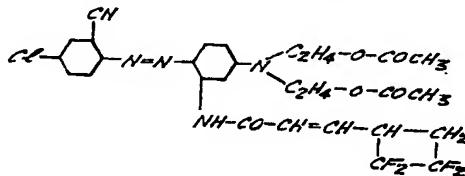


is obtained, which dyes wool yarn orange shades.

Example 3

3.1 Parts of 2-cyano-4-chloro-aniline are introduced into 20 parts by volume of 2N hydrochloric acid. Diazotisation is carried out with 4N sodium nitrite solution at a temperature of 0 to 5°C and the mixture is stirred for some time. Thereafter the excess nitrite is destroyed with urea.

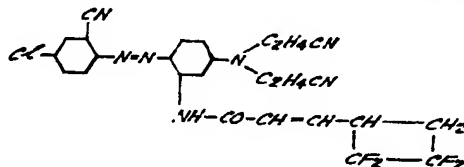
This solution is added dropwise, at a temperature of at most 10°C, to a solution of 9.2 parts of N-bis-β-acetoxyethyl-3-[β-(2',2',3',3'-tetrafluorocyclobutyl-acryl)-amido]-aniline in 125 parts of 80% acetic acid, the mixture is stirred overnight at 0 to 10°C and the dyestuff is precipitated by adding ice water. After filtering, the dyestuff is washed until neutral and dried *in vacuo*. A dyestuff of the formula



is obtained which dyes nylon fibres yellowish-tinged red shades of excellent fastness to washing.

Example 4

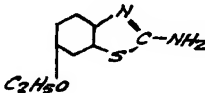
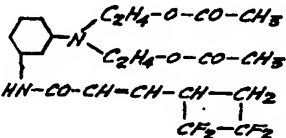
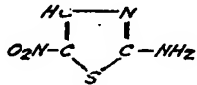
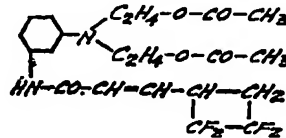

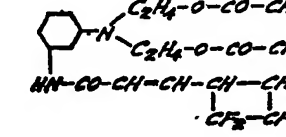
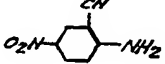
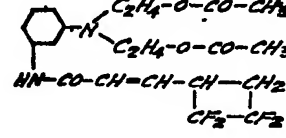
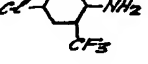
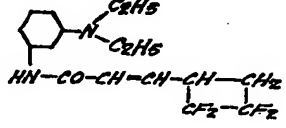

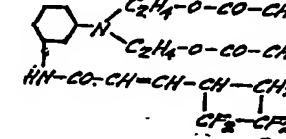
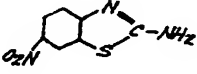
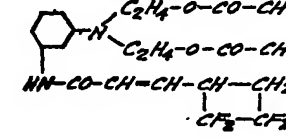
5 When instead of the above-mentioned N-bis-β-acetoxyethyl-3-[β-(2',2',3',3'-tetrafluorocyclobutyl-acryl)-amido]-aniline 7.9 parts of N-bis-β-cyanethyl-3-[β-2',2',3',3'-tetrafluorocyclobutyl-acryl)-amido]-aniline are used, a dyestuff of formula



is obtained which dyes wool fibres orange-red shades.

10 When the diazo compounds of the amines mentioned in column I are coupled with the coupling components mentioned in column II under the conditions mentioned in Example 1, reactive dispersion dyestuffs are obtained which dye polyamide fibres the shade given in column III, provided no other type of fibre is mentioned.

10

| No. | I | II | III |
|-----|---|--|-----------------------|
| 1 |  |  | reddish-tinged violet |
| 2 |  |  | blue |
| 3 |  |  | red |
| 4 |  |  | violet |
| 5 |  |  | red |
| 6 |  |  | red |
| 7 |  |  | violet |

| No. | I | II | III |
|-----|---|----|-----------------------|
| 8 | | | red |
| 9 | | | orange red |
| 10 | | " | violet on polyester |
| 11 | | " | red |
| 12 | | | red |
| 13 | | " | red |
| 14 | | | reddish-tinged violet |
| 15 | | | orange-yellow |
| 16 | | | orange |

| No. | I | II | III |
|-----|---|----|----------------|
| 17 | | | reddish-orange |
| 18 | " | | orange |
| 19 | | | orange red |
| 20 | " | | golden yellow |
| 21 | | | orange red |
| 22 | " | | orange |
| 23 | | | violet |

| No. | I | II | III |
|-----|---|----|----------------------------------|
| 24 | | | orange |
| 25 | | | orange |
| 26 | | | scarlet |
| 27 | | | scarlet |
| 28 | | | bluish-tinged red (on polyester) |
| 29 | | | bluish-tinged red (on polyester) |
| 30 | | | bluish-tinged red |
| 31 | | | violet |

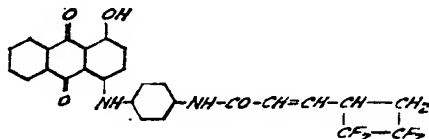
| No. | I | II | III |
|-----|--------------------------|----|--------------------------|
| 32 | | | yellow orange |
| 33 | | 33 | orange red |
| 34 | | | yellow orange |
| 35 | 4-Nitro-aniline | | red |
| 36 | 2-Chloro-4-nitro-aniline | | bluish-tinged red |
| 37 | 2-Cyano-4-chloraniline | | yellowish- tinged red |
| 38 | 2-Chloro-4-nitro-aniline | | yellowish- tinged red |

| No. | I | II | III |
|-----|------------------------------------|----|----------------------|
| 39 | 2-Chloro-4-methylsulphonyl-aniline | | orange |
| 40 | 2-Chloro-4-methylsulphonyl-aniline | | orange (on wool) |
| 41 | 2-Cyano-4-chloraniline | | yellowish-tinged red |
| 42 | " | | yellowish-tinged red |
| 43 | " | | yellowish-tinged red |
| 44 | 4-Nitro-aniline | | red |
| 45 | 2-Cyano-4-nitro-aniline | | violet |

| No. | I | II | III |
|-----|-------------------------------------|----|----------------------|
| 46 | 2-Cyano-4-chloraniline | | yellowish-tinged red |
| 47 | 2-Cyano-4-chloraniline | | yellowish-tinged red |
| 48 | 2-Chloro-4-nitro-aniline | | bluish-tinged red |
| 49 | 2-Trifluoromethyl-4-chlor-aniline | | orange red |
| 50 | 2,5-Dimethoxy-4-cyan-aniline | | red |
| 51 | 2-Chloro-4-methyl-sulphonyl-aniline | | orange |
| 52 | 4-Aminosulphonyl-aniline | | yellow orange |
| 53 | 2-Cyano-4-chloraniline | | orange |
| 54 | 2-Chloro-4-methyl-sulphonyl-aniline | 33 | orange |

Example 5

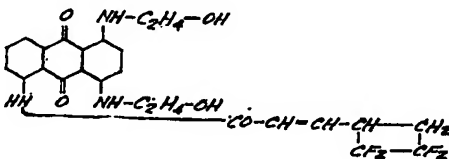
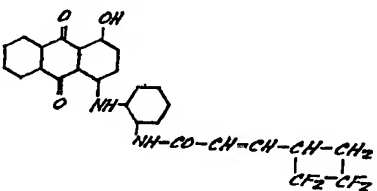
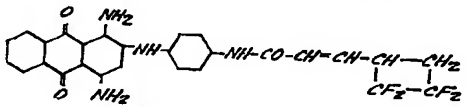
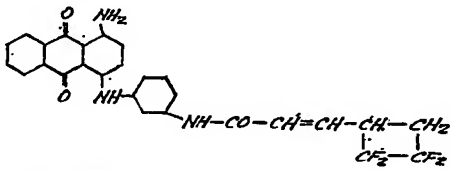
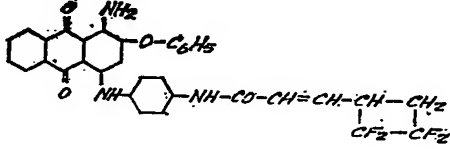
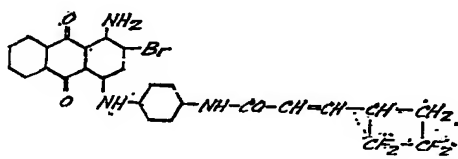
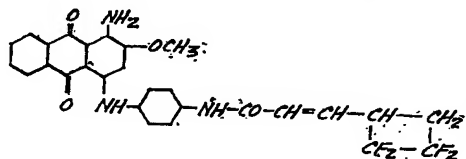
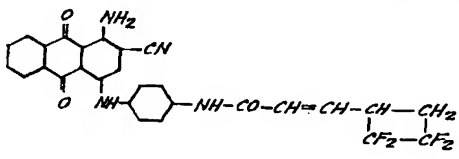
5 4 Parts of 1-hydroxy-4-[(*p*-aminophenyl)-amino]-anthraquinone are suspended in 50 parts by volume of glacial acetic acid. A slight excess of β -(2,2,3,3-tetrafluorocyclobutyl)-acrylic acid chloride is added thereto and the suspension is stirred for some time. Thereafter the mixture is poured into ice water and filtered, and the residue is well washed with water. After drying *in vacuo*, a dyestuff of the formula



is obtained, which dyes nylon fibres blue shades.

The following dyestuffs are obtained in an analogous manner, starting from the appropriate amino anthraquinones:

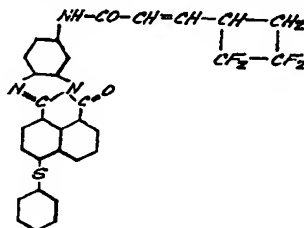
| | | Shade on Polyamide |
|---|--|--------------------|
| 1 | | yellow |
| 2 | | orange red |
| 3 | | golden yellow |
| 4 | | scarlet |
| 5 | | blue |
| 6 | | blue |

| | | Shade on Polyamide |
|----|--|----------------------|
| 7 |  | blue |
| 8 |  | blue |
| 9 |  | blue |
| 10 |  | blue |
| 11 |  | violet |
| 12 |  | violet |
| 13 |  | violet |
| 14 |  | greenish-tinged blue |

| | | Shade on Polyamide |
|----|--|---------------------|
| 15 | | bluish-tinged green |
| 16 | | blue |
| 17 | | blue |
| 18 | | blue |
| 19 | | blue |
| 20 | | blue |
| 21 | | blue |
| 22 | | bluish-tinged red |

Example 6

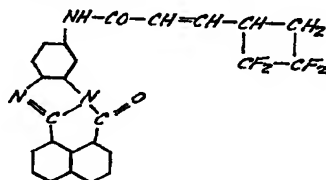
A slight excess of β -(2,2,3,3-tetrafluorocyclobutyl)-acrylic acid chloride is added dropwise at room temperature to a suspension of 3.9 parts of 4'-phenylthio-1,2-naphthoylene-4-amino-benzimidazole in 80 parts of glacial acetic acid; the mixture is stirred overnight and the dyestuff is precipitated by adding ice water. After filtering, the dyestuff is washed until neutral and dried *in vacuo*. A dyestuff of the formula



is obtained which dyes polyamide and polyester fibres golden yellow shades having good general fastness properties.

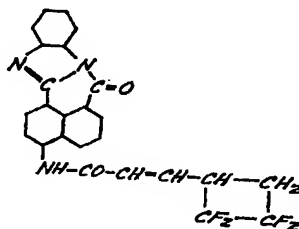
Example 7

11.4 parts of 4-amino-naphthoylene-benzimidazole are suspended in 160 parts of glacial acetic acid. A slight excess of β -(2,2,3,3-tetrafluorocyclobutyl)-acrylic acid chloride is added dropwise at 25°C, the mixture is warmed to 40–45°C and stirred overnight, and the dyestuff is precipitated by adding ice water, filtered, washed until neutral and dried *in vacuo*. A dyestuff of the formula



is obtained which dyes polyamide and polyester fibres greenish-tinged yellow shades.

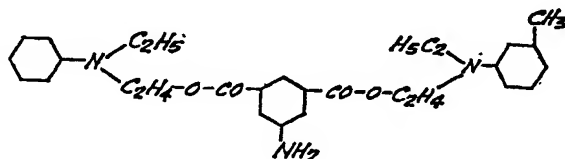
The following dyestuff is similarly obtained starting from the corresponding aminoperinone:



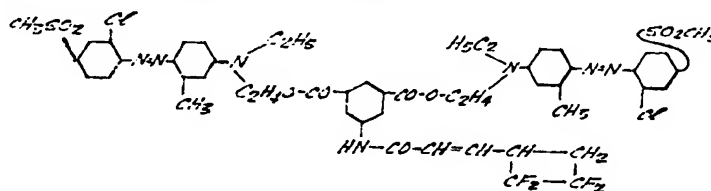
shade on polyamide: yellow

Example 8

2.3 Parts of 3-chlor-4-amino-phenylenemethylsulphone (90.5%) are diazotised at 20 to 25°C with 100 parts by volume of 0.5 N nitrosylsulphuric acid, the mixture is stirred for 1 hour and then diluted with 20 parts by volume of a mixture of glacial acetic acid/propionic acid (6:1). This diazo solution is added dropwise at 0 to 5°C to a solution of 3.6 parts of the amine of the formula



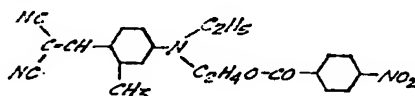
in 100 parts by volume of glacial acetic acid/propionic acid, 6:1. After 3 hours the coupling has finished. The dyestuff of the formula



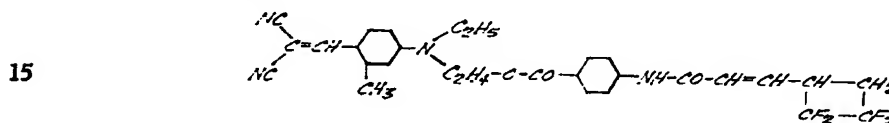
5 is precipitated by adding sodium acetate solution, filtered off, washed until neutral and dried. An orange-red product is obtained which dyes nylon fibres red shades. 5

Example 9

4 parts of the product of the formula

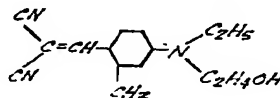


10 are hydrogenated in acetonitrile using a catalyst consisting of 10% palladium on charcoal, until the amount of hydrogen required for the reduction of the nitro group has been taken up. Starting material is no longer detectable in the thin layer chromatogram. The acetonitrile is distilled off and the residue, in glacial acetic acid, is reacted with a slight excess of β -(2,2,3,3-tetrafluorocyclobutyl)-acrylic acid chloride. The dyestuff of the formula 10

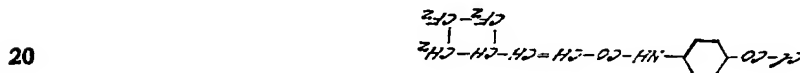


15 is obtained, which dyes nylon fibres greenish-tinged yellow shades. 15

The same dyestuff is also obtained by acylation of the product of the formula

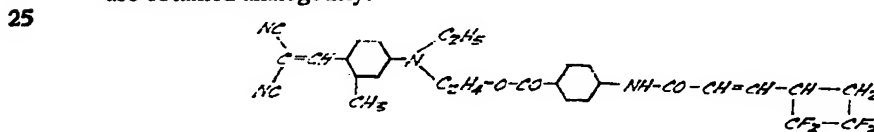


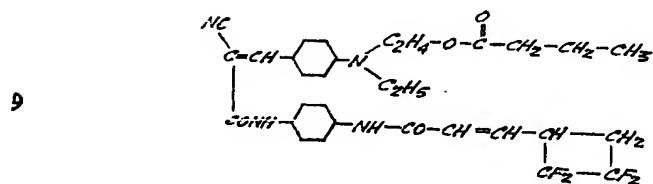
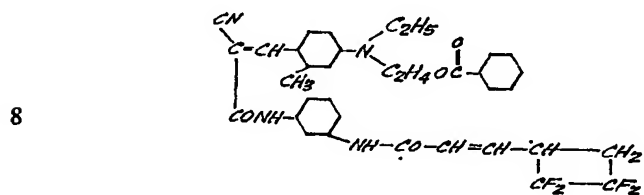
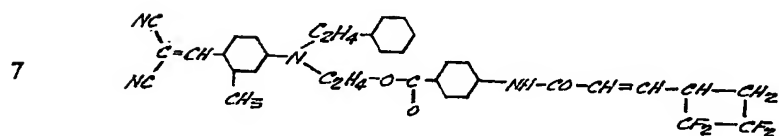
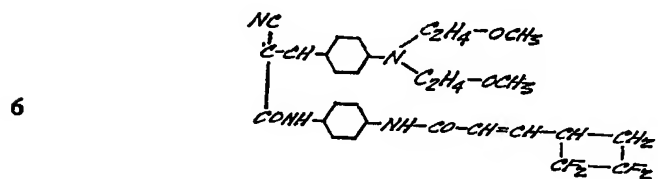
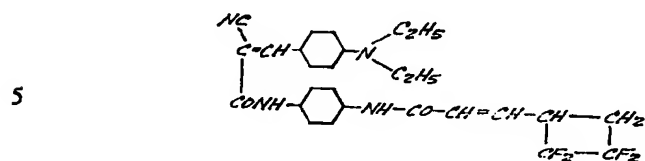
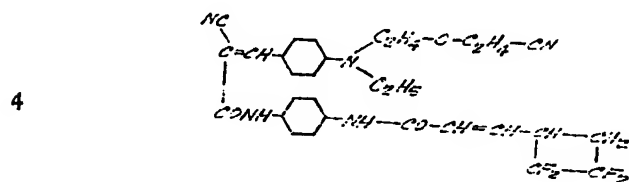
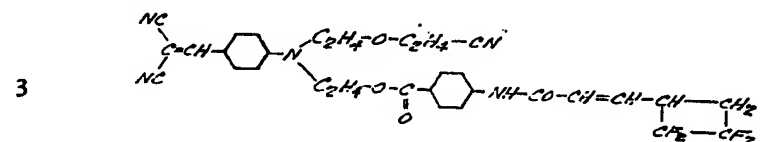
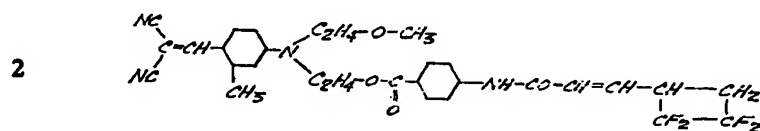
with the acid chloride of the formula



20 This acid chloride was obtained by acylation of *p*-aminobenzoic acid with β -(2,2,3,3-tetrafluorocyclobutyl)-acrylic acid chloride and subsequent reaction with thionyl chloride. 20

The following dyestuffs, which all dye polyamide greenish-tinged yellow shades, are obtained analogously.



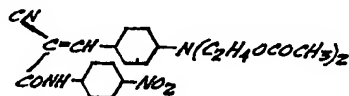


Example 10

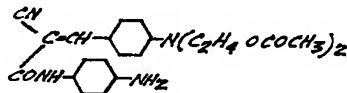
Condensation of *p*-nitroaniline with cyanoacetic acid chloride in toluene yields the compound of the formula



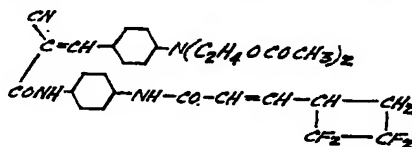
- 5 4.3 parts of this product, in 50 parts by volume of methanol and 5 drops of piperidine, are condensed with 5.9 parts of *N,N*-di- β -acetoxyethyl-*p*-aminobenzaldehyde. The product of the formula



- 10 is obtained in good yield. Catalytic reduction thereof with Raney nickel in dimethylformamide until the amount of hydrogen required for the reduction of the nitro group has been taken up yields the product of the formula



- 15 2.25 parts of this product, in 20 parts by volume of glacial acetic acid are mixed at 15–20°C with a slight excess of β -(2,2,3,3-tetrafluorocyclobutyl)-acrylic acid chloride and stirred for 20 hours at 15 to 20°C. The dyestuff of the formula

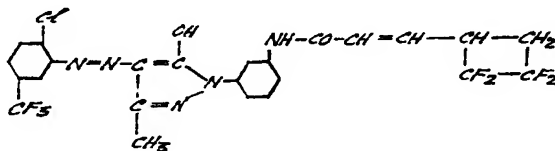


is filtered off, washed with methanol and dried. It dyes polyamide fibres vivid greenish-tinted yellow shades.

Example 11

- 20 19.55 Parts of 3-amino-4-chlorobenzotrifluoride are diazotised in the usual manner and coupled with 19 parts of 1-(3'-aminophenyl)-3-methyl-5-pyrazolone. The new monoazo dyestuff is isolated and dried.

- 25 19.77 Parts of the dyestuff are stirred with 200 parts of toluene and treated dropwise at 60°C with a slight excess of β -(2,2,3,3-tetrafluorocyclobutyl)-acrylic acid chloride in 20 parts of toluene during 20 minutes. Thereafter the mixture is heated to 60°C and stirred for 6 hours. After cooling, the new dyestuff of the formula



is isolated, washed with petroleum ether and dried. It is a yellow powder which dyes polyamide fibres attractive yellow shades having very good fastness properties.

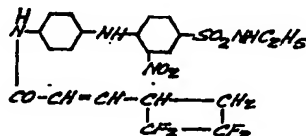
- 30 A dyestuff with the same good properties is obtained when 1-(4'-aminophenyl)-3-methyl-5-pyrazolone is used as the coupling component.

Example 12

33.6 Parts of 4'-amino-3-nitro-diphenylamine-1-sulphonic acid-*N*-ethylamide are dissolved in glacial acetic acid and stirred with a slight excess of β -(2,2,3,3-tetrafluoro-

cyclobutyl)-acrylic acid chloride until the reaction is complete. The dyestuff is then precipitated by adding water, isolated and dried *in vacuo*.

The dyestuff of the formula

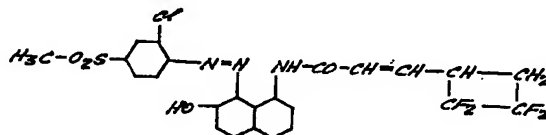


5 when is sparingly soluble in water but soluble in organic solvents is a yellow powder which dyes polyamide fibres yellow shades having very good wet fastness properties. 5

Example 13

20.55 Parts of 4-amino-3-chlorophenyl-methyl-sulphone are diazotised and coupled at 0 to 5°C with 37.3 parts of 1-[β-(2',2',3',3'-tetrafluorocyclobutyl)-acryl- amino]-7-hydroxynaphthalene in a weakly alkaline medium to give the monoazo dyestuff. 10

The dyestuff of the formula



15 which is insoluble in water but soluble in organic solvents is isolated and dried *in vacuo*. It is a dark powder which dyes polyamide fibres and wool fibres luminous scarlet-red shades having especially good wet fastness properties. 15

Example 14

20 5.9 Parts of 5-amino-1,9-pyrazolanthrone are suspended in chlorobenzene. A slight excess of β-(2,2,3,3-tetrafluorocyclobutyl)-acrylic acid chloride is added dropwise at room temperature and the mixture thereafter heated to 80°C and stirred for some time. It is then allowed to cool, and the product is filtered off and washed with cold chlorobenzene. After drying *in vacuo* the N-β-(2',2',3',3'-tetrafluorocyclobutyl)-acrylamide of 5-amino-1,9-pyrazolanthrone, which dyes polyamide yellow shades, is obtained. 20

Example 15

25 10 Parts of nylon-6,6-tricot fabric ["Helanca" (a registered Trade Mark)] are introduced at 30°C into a dyebath which in 400 parts by volume of water contains 8 parts of sodium bicarbonate and 2 parts of a 5% aqueous dispersion of the dyestuff obtained according to Example 1, and which has a pH-value of 7.9. The mixture is heated to the boil during 45 minutes and dyeing is then carried out for 75 minutes at the boil. Thereafter the textile material is well rinsed with water and dried. An orange dyeing is obtained. 30

Example 16

35 Dyeing of 10 parts of polyester-tricot fabric [texturised polyester woven fabric "Crimplene" (a registered Trade Mark)] is started at 30°C in a high temperature dyeing apparatus, with a dyebath which in 400 parts of water contains 0.8 part of an adduct of 9 mols of ethylene oxide and 1 mol of nonylphenol and 2 parts of a 5% dispersion of the dyestuff described in Example 1. The pH-value of the liquor is 7.0. The temperature is raised to 120°C in 15 minutes, during which a pressure of about 2 atmospheres excess is produced. Dyeing is carried out for 45 minutes at 120°C and thereafter the mixture is cooled to 65°C during 10 minutes. The textile material is then rinsed cold and dried. An orange dyeing is obtained. 40

Example 17

45 10 Parts of nylon-6,6-tricot fabric ["Helanca" (a registered Trade Mark)] are introduced at 30°C into a dyebath which in 400 parts by volume of water contains 0.2 part of 80% acetic acid and 2 parts of a 5% aqueous dispersion of the dyestuff obtained according to Example 1, and which has a pH-value of 4 to 5. The mixture is 45

heated to the boil during 45 minutes and dyeing is then carried out for 30 minutes at the boil. Thereafter a pH-value of 12 is established by adding sodium carbonate and boiling continued for 30 minutes. After this the textile material is well rinsed with water and dried. An orange dyeing with a high proportion of non-extractable dyestuff is obtained.

Example 18

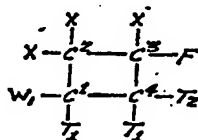
Dyeing is carried out as in Example 16 but a polyacrylonitrile high bulk tricot fabric (high bulk "Orlon"-tricot) is used. ("Orlon" is a registered Trade Mark). An orange dyeing is obtained.

The dyestuff dispersions used above are obtained by grinding 20 parts of dyestuff with 140 parts of water and 40 parts of sodium dinaphthylmethane disulphonate.

WHAT WE CLAIM IS:—

1. Reactive dyestuffs free from acidic groups conferring solubility in water which contain at least one fibre-reactive acyl residue Z of a halogenated cyclobutane containing a carboxylic acid amide or sulphonic acid amide group bound to the remainder of the dyestuff molecule through the nitrogen atom.

2. Reactive dyestuffs as claimed in claim 1, wherein the group Z is a group of the formula



in which T₁ and T₂ each represents a chlorine atom or a cyano or nitro group or a grouping —T', —OT', —COOT'', —SO₂NT'T'', —SO₂T' or —CO—NT'T'', and the two symbols T₁ can jointly represent a further carbon bond between the carbon atoms C₁ and C₄, and wherein T' and T'' each represents a hydrogen atom or an alkyl, aralkyl or aryl group, T''' represents an alkyl or aryl group and X represents a hydrogen or halogen atom, the group Z being bound to the dyestuff molecule through a group —NT'— and through W₁ which represents one of the groupings —CO—, —SO₂—, —SO₂—CH₂—CH₂—, —CO—CH=CH— or —CO—CHT''—CHT'—,

and wherein the two T₁ groups and the X atoms may be the same or different.

3. Reactive dyestuffs as claimed in claim 2, wherein X represents a fluorine or chlorine atom.

4. Reactive dyestuffs as claimed in any one of claims 1 to 3, which contain a 2,2,3,3-tetrafluorocyclobutyl (carbonyl- or acryloyl) residue bound to an amino group.

5. Reactive dyestuffs as claimed in any one of claims 1 to 4, which are azo dyestuffs.

6. Reactive dyestuffs as claimed in claim 5, which are monoazo dyestuffs.

7. Reactive dyestuffs as claimed in claim 5, which are disazo dyestuffs.

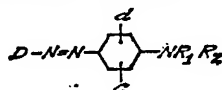
8. Reactive dyestuffs as claimed in any one of claims 1 to 4, which are anthraquinonoid dyestuffs.

9. Reactive dyestuffs as claimed in any one of claims 1 to 4, which are styryl dyestuffs.

10. Reactive dyestuffs as claimed in any one of claims 1 to 4, which are perinones, quinophthalones or nitro dyestuffs.

11. Monoazo dyestuffs as claimed in claim 6, which correspond to the formula D—N=N—A—NR₁R₂, wherein D represents the residue of a diazo component, A represents an 1,4-phenylene residue that may be substituted and R₁ and R₂ each represents an alkyl group that may be substituted, at least one of the residues D, A, R₁ and R₂ containing a fibre-reactive residue Z bound to an amino group, wherein Z has the meaning given in claim 2.

12. Monoazo dyestuffs as claimed in claim 11, which correspond to the formula

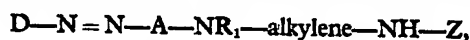


wherein d is a hydrogen atom, a bromine or chlorine atom, a lower alkyl, alkylmercapto or alkyloxy residue, a phenoxy, phenylmercapto or phenyl residue which may contain as substituents chlorine, bromine, lower alkyl or lower alkoxy residues and c is the same or a trifluoromethyl group or a non-fibre-reactive acylamino residue wherein the acyl

residue is derived from a carboxylic acid, an organic monosulphonic acid, a carbonic acid mono ester or a carbamic ester, or a fibre-reactive residue —NH—Z .

13. Dyestuffs as claimed in claim 11, wherein the group A carries a group —Z bound via an amino group in the ortho-position to the azo group.

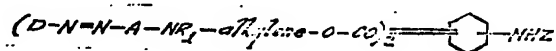
14. Dyestuffs as claimed in claim 11, which correspond to the formula



wherein the alkylene residue contains up to 3 carbon atoms.

15. Dyestuffs as claimed in claim 11, wherein D is an unsubstituted or substituted monocyclic or bicyclic heterocyclic diazo component of the thiazole, benzothiazole, imidazole, thiadiazole or isothiazole series or a diazo component of the benzene series.

16. Dyestuffs as claimed in claim 7 of the formula



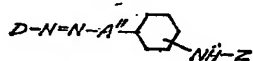
wherein D represents the residue of a diazo component, A is a *p*-phenylene residue that may be substituted and R_1 is an alkyl group that may be substituted.

17. Dyestuffs as claimed in claim 6 of the formula



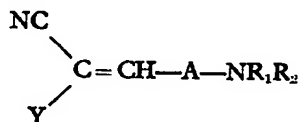
wherein D is a residue of a diazo component and R is a hydroxynaphthalene residue.

18. Dyestuffs as claimed in claim 6 of the formula



wherein D is a residue of a diazo component and A'' is a pyrazolone radical.

19. Dyestuffs as claimed in claim 9, which correspond to the formula



wherein A, R_1 and R_2 have the meanings given in claim 11 and Y is a cyano, carbalkoxy, carboxylic acid amide or arylsulphonyl group, wherein at least one of the groups A, R_1 and R_2 contains the group —NH—Z .

20. Dyestuffs as claimed in claim 19, wherein Y is a carbethoxy or phenylsulphonyl group.

21. Dyestuffs as claimed in claim 19, wherein Y has the formula

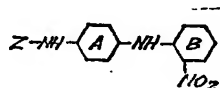


22. Dyestuffs as claimed in claim 19, wherein R_2 has the formula



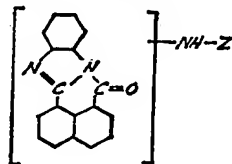
wherein Y represents —O— or —NH— .

23. Dyestuffs as claimed in claim 10 of the formula



wherein the nucleus B may be substituted.

24. Dyestuffs as claimed in claim 10 of the formula



which may be substituted.

25. Dyestuffs as claimed in claim 8, which correspond to the formula

5



5

wherein n is 1 or 2, Z has the meaning given above and A' represents a residue of the anthraquinone series having 3 to 5 condensed rings, which contain one or more other substituents, and R is a hydrogen atom or an alkyl group.

26. Dyestuffs as claimed in claim 25, which correspond to the formula

10



10

wherein n is 1 or 2, m is 1 or 2, A'' is an anthraquinone, thiazoleanthrone, pyrazoleanthrone or phthaloylacridone, X is alkylene or arylene, and Y is $-O-$ or $-NH-$; with the proviso that the $-CO-$ can be attached only in a β -position of the anthraquinone nucleus.

15

27. Dyestuffs as claimed in claim 1, obtained substantially as described in any one of the Examples 1 to 14 or with reference to the Tables herein.

15

28. A process for the manufacture of reactive dyestuffs as claimed in claim 1, wherein either a diazotised amine is coupled with a coupling component and one of the two components contains at least one of the fibre-reactive groups indicated in claim 1, or a dyestuff containing an acylatable amino group is acylated with an anhydride or halide of a carboxylic or sulphonic acid containing a halogenated cyclobutane ring.

20

20

29. A process as claimed in claim 28, wherein the fibre-reactive residue of the cyclobutane derivative has the formula given in claim 2.

25

30. A process as claimed in claim 29, wherein a 2,2,3,3-tetrafluorobutyl-(carbonyl or acryloyl) residue is introduced.

25

31. A process as claimed in any one of claims 28 to 30, wherein the acylatable amino group, which is present in the starting dyestuff is acylated with an acid halide or acid anhydride of the fibre-reactive cyclobutane derivative in an organic solvent.

30

32. A process as claimed in any one of claims 28 to 31, wherein a 2,2,3,3-tetrafluorocyclobutane-1-carboxylic acid halide is used as the acylating agent.

30

33. A process as claimed in any one of claims 28 to 32, wherein the starting dyestuff possesses at least one free $-NH_2$ group.

35

34. A process as claimed in any one of claims 28 to 33, wherein the starting dyestuff is an anthraquinone dyestuff having 3 to 5 condensed rings.

35. A process as claimed in claim 34, wherein the starting dyestuff is an anthraquinone, a thiazoleanthrone, a pyrazoleanthrone or a phthaloylacridone dyestuff.

35

36. A process as claimed in any one of claims 28 to 33, wherein the starting dyestuff is a perinone or a nitro dyestuff.

40

37. A process as claimed in any one of claims 28 to 30, wherein the dyestuff is manufactured by coupling a diazonium compound with a coupling component which contains the fibre-reactive residue of the cyclobutane derivative.

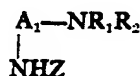
40

38. A process as claimed in claim 37, wherein a coupling component of formula $H-A-NR_1-R_2-NH-Z$ wherein R_1 is an alkyl group, R_2 an alkylene group and A a p -phenylene residue is coupled with a diazonium compound.

45

39. A process as claimed in claim 37, wherein a coupling component of the formula

45



wherein A_1 is a m -phenylene residue and R_1 and R_2 are alkyl groups that may be substituted, is coupled with a diazonium compound.

40. A process as claimed in claim 28, conducted substantially as described in any one of the Examples 1 to 14 or with reference to the Tables herein.
41. Compounds as claimed in claim 1, whenever prepared by a process claimed in any one of claims 28 to 40.
- 5 42. A process for dyeing and printing synthetic fibres, wherein a dyestuff claimed in any one of claims 1 to 27 or 41 is used. 5
43. A process as claimed in claim 42, wherein the synthetic fibres are fibres containing amino, amide and/or ester groups.
44. Material whenever dyed or printed by a process claimed in claim 42 or 43.
- 10 45. A process for dyeing or printing polyamides, wherein a dyestuff claimed in any one of claims 1 to 27 or 41 is used. 10
46. A process as claimed in claim 45, wherein the polyamide is wool.
47. Material whenever dyed or printed by a process claimed in claim 45 or 46.
- 15 48. A process for dyeing or printing fibres containing ester groups, wherein a dyestuff claimed in any one of claims 1 to 27 or 41 is used. 15
49. A process as claimed in claim 42, wherein the fibres are linear polyester fibres.
50. Material whenever dyed or printed by a process claimed in claim 47 or 48.
51. A process as claimed in any one of claims 42, 45 or 48 conducted substantially as described and exemplified herein.
- 20 52. A dyeing preparation which contains a dyestuff claimed in any one of Claims 1 to 27 and 41. 20
53. A preparation as claimed in claim 52 substantially as described and exemplified herein.

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